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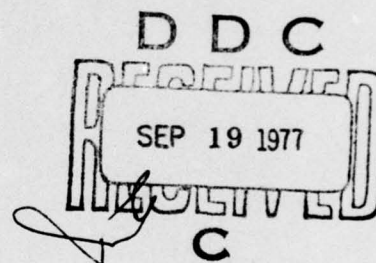
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Electron Resists

by
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APRIL 1977

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R. G. Freeman, III, RAdm., USN Commander

G. L. Hollingsworth Technical Director

FOREWORD

This report covers a survey of electron-beam resist materials. Work was authorized under Contract No. 5525-6880-76. Work on this survey was performed between January 1976 and January 1977. This is a final report.

This report was reviewed for technical accuracy by G. Turner.

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(U) This report is a survey of the work on electron-beam resist materials as reported in the open literature. The period surveyed does not go beyond 1 January 1977.

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INTRODUCTION

Silicon integrated circuit fabrication is heavily dependent upon the selective etching of thin dielectric and conductor films. This is accomplished by protecting the areas which do not require removal with a polymer film, termed a resist. The resist is patterned by altering its solubility by exposing it with energetic irradiation and subsequently dissolving (developing) the unwanted areas of the polymer. A resist that becomes less soluble after irradiation is defined as a negative resist, and, conversely, if the solubility increases it is denoted a positive resist.

Photolithography is a process presently used to fabricate most microelectronic devices. This technique, utilizing flood exposure through a mask carrying the designated pattern, requires a few minutes with a rather inexpensive exposure system. Due to the long wavelengths that are employed (3000 to 4000 Å) and other optical and process limitations, features of 2 to 4 μm are the smallest that can be readily delineated.

Requirements for devices with faster switching frequencies and higher packing densities have created a need for higher resolution patterns ($< 1.0 \mu\text{m}$), accompanied with higher yields. Pattern delineation using a focused beam of electrons has been shown to be a useful technique for producing features of less than 1000 Å (References 1-4). Since the late 1960s electron lithography has gained rapid acceptance as a technique of great potential for fabricating large scale, high resolution, integrated circuits. Advantages other than high resolution offered by electron lithography are direct computer controlled pattern generation, precise line width control of conventional size features (useful in master-mask production), and lower defects in the finished product.

It is apparent that, for either scanning or projection electron lithography to be fruitful, families of both positive and negative electron resists must be available with properties designed to maximize advantages offered by this new technology.

BASIC CONCEPTS AND THEORETICAL ASPECTS OF ELECTRON RESIST DESIGN

POSITIVE AND NEGATIVE RESISTS, GENERAL DEFINITION

High polymers undergo physical and chemical change under ionization radiation. The most important fact pertaining to their use as resists is that both crosslinking and scission of polymer chains occur. In many cases one dominates the other, and a polymer either crosslinks or degrades, depending on its nature. When a crosslinking polymer film that is coated on a surface is exposed selectively to an electron beam, the irradiated portion crosslinks. With a sufficient dose the crosslinked polymer forms a three-dimensional network, its molecular weight increases, and it becomes insoluble in the usual solvent

for that polymer. The film can be "developed" by immersing it in the solvent to dissolve away the unexposed polymer film, leaving a three-dimensional network of the polymer in the exposed area. A crosslinking polymer is a negative electron resist if the crosslinked polymer is unaffected by the etching solution.

When a degrading polymer film is exposed to an electron beam, random scission occurs and the average molecular weight decreases. The degraded polymer may dissolve in a solvent in which the original polymer is not soluble. During development the exposed film is washed away leaving the unexposed film on the surface. If the original polymer is unaffected by the etching solution, the polymer is a positive resist.

The behavior of a polymer during irradiation can often be predicted from the structure of the monomer unit in the polymer (Reference 5). The general rule is that if the carbon atoms in the main chains of the polymer carry at least one hydrogen atom, the polymer will crosslink upon irradiation. If a tetrasubstituted carbon atom is present in the monomer unit, the polymer tends to degrade.

GLASS TRANSITION TEMPERATURE

An important characteristic of a polymer is its glass transition temperature, T_g . Above this temperature the polymer chains can slide over each other and the polymer becomes soft, pliable, and rubber-like. Below this temperature the atoms can only vibrate about their equilibrium positions at fixed distances from each other. In this case the chains cannot slide over each other, and the polymer becomes hard, brittle, and glass-like. Under stress a polymer deforms easily at temperature T above T_g . An exposed and developed film will change its shape if it has some residual stress, will not maintain its definition, and will not be suitable for high resolution applications (Reference 2). Such loss of resolution due to creep in a polymer film may be minimized by prebaking the coated film at a temperature above T_g to relax the stress created in the film during coating and by storing the film at a temperature below T_g . In developing an exposed positive resist not only the polymer fragments in the exposed area will be removed, but also some smaller molecules in the unexposed area (Reference 6). If the development is performed at a temperature above T_g , this will increase the probability of pinhole formation. However, below T_g the polymer chains cannot slide along each other, and small molecules are not easily extracted, being held rigidly by other molecules. Similarly, if an exposed negative resist is developed at temperature above T_g , some small three-dimensional networks may be extracted away. This extraction will be much less likely if the film is developed at a temperature below T_g . After development, holes or discontinuities may be formed in the film and along the edge of the developed film vacated by the extracted molecules. These holes may be closed if the film is baked at a temperature above T_g . Therefore, a resist film should be prebaked at $T > T_g$, exposed and developed at $T < T_g$, postbaked at $T > T_g$, and stored at $T < T_g$. As the resist is usually processed and stored at room temperature, T_g of the polymer must be above room temperature, preferably above 350°K. Among polymers that are known to crosslink or degrade by scission, only a few have reasonably high glass transition temperature. The number of polymers that can be used as high resolution resists is therefore rather limited.

RADIATION CHEMICAL EFFICIENCY

Electrons that are used to induce chemical reactions in resist materials have hundreds or even

thousands of times more energy than that associated with chemical bonds. The electron-chemical bond interaction is thus somewhat nonspecific and not strictly analogous to photochemical reactions utilized in photolithography. Every bond in a polymer that is exposed to 5,000 to 20,000 electron volts is susceptible to rearrangement or destruction, and the radiation chemistry is far more complicated in terms of predicting specific mechanisms. The best approach is that developed by Charlesby (Reference 7) where overall chemical effects are discussed in terms of "G" values (radiation chemical efficiency) which are not dependent on any specific detailed mechanisms. Two reactions of interest that may occur, crosslinking and/or chain scission, are characterized by the parameters G_{scission} ($G(s)$) or $G_{\text{crosslinking}}$ ($G(c)$), defined as the number of crosslinks formed or chains broken per 100 electron volts of energy absorbed. Both scission and crosslinking occur simultaneously at varying rates in every polymer system undergoing irradiation. For a negative resist, $G(c)$ should be as large as possible for the highest sensitivity and $G(s)$ a minimum for the highest contrast. Conversely, for a positive resist $G(s)$ should be maximum and $G(c)$ a minimum. G values were obtained with either gamma-ray or MEV-electron irradiations on bulk samples. Hatzakis and Ting (Reference 8) described a way to determine the G value for positive resist film under typical electron microfabrication conditions.

ELECTRON SCATTERING

Although electron beams of reasonable current density can be focused easily to diameters of less than 0.05 μm , maximum resolution is seldom realized in practice because of electron scattering both from the substrate and in the resist (Reference 9). When an electron beam enters a thin polymer film on a substrate, electrons lose energy as they undergo elastic and inelastic collisions. During these processes, other quanta of energy are produced (Reference 10): secondary and backscattered electrons, and X-rays and thermal energy, all of which can result in chemical reactions. It is the total distribution of all forms of energy as a function of location from the primary beam that becomes an important parameter when high resolution electron lithography is considered. Although backscattering from the substrate contributes to line broadening, particularly with substrates of high atomic number such as Ni, W, or Au (Reference 11), of equal importance are inelastically scattered electrons which create a flux of electrons essentially perpendicular to the primary beam (References 11-13). Two factors are important in determining the effect of these scattered electrons: first, the rate at which the electron loses energy (dV/dZ); and second, the electron current at every point in the resist. Some additive function of these two factors describes their effect on a polymer resist at any distance from the primary beam (References 14 and 15). Heidenreich *et al* (Reference 13) developed a depth-dose model for the penetration of electrons in a thin polymer film on a substrate. Their model is used to correlate the effects of accelerating voltage, resist thickness, resist sensitivity, and contrast on resolution. The plot of film thickness remaining as a function of log dose, expressed in $\text{C}\cdot\text{cm}^{-2}$, is referred to as the thickness-dose curve for a negative resist and characterizes the response of the resist to electron irradiation. The plot of film thickness removed as a function of log dose is referred to as the thickness-dose curve for a positive resist.

ELECTRON RESIST DESIGN

In designing an electron resist, it is important to understand various physical and chemical properties of a polymer on ultimate resist performance in terms of the specific requirements for an electron resist.

Sensitivity

Resist sensitivity is conventionally taken as the input-electron dose in $\text{C}\cdot\text{cm}^{-2}$ required to achieve the necessary chemical response in the resist. The necessary resist response is usually a faithful replication in the developed resist pattern of the "original" pattern specified by the circuit designer. The sensitivity required of an electron resist will depend on the application and type of writing machine to be used. Projection systems require lower sensitivity materials than scanning systems. For scanning systems it is desired that the sensitivity not be the limiting factor on writing speed. Sensitivity data for both negative and positive resists must include resist thickness before and after development, beam accelerating voltage, developed image resolution, developer solution, and development time. Electron induced reactions of polymers are nonspecific and similar to thermally induced reactions. It has been found that thermal resist sensitivity is generally proportional to electron sensitivity (Reference 10), and hence polymers with high electron sensitivities may have low thermal stabilities. Thus, resists with sensitivities greater than approximately $10^{-8} \text{ C}\cdot\text{cm}^{-2}$ tend to be thermally unstable and lead to difficulties in preparation, and processing resists with sensitivities less than approximately $10^{-5} \text{ C}\cdot\text{cm}^{-2}$ are not generally sensitive enough.

Contrast

Contrast is a measure of the chemical response of a resist to input dose. High contrast value implies very rapid changes in resist response to small changes in input dose. The contrast value is usually taken as the slope of the thickness-dose curve. Low contrast resists require considerable exposure beyond the minimum incident dose necessary to form an image after development to achieve a useful thickness. This results in large lateral currents that reduce resolution. So, resists with higher contrast values are desirable because they respond only over a limited range of dose and are thus less affected by the lateral dose distributions set up within the resist by scattering or diffraction of the incident radiation (References 10, 13, and 16). High contrast generally implies a steep edge profile and high resolution capability in the developed resist patterns (Reference 17), since response to low dose levels between adjacent features is minimized. In order to give direct information on line widths, Brewer (Reference 18) defined the "line width contrast" of the resist as the ratio between a change in log dose to a change in normalized line width. He mentioned that it appears generally true that the contrast is not related to the speed of the resist. The contrast is related to the efficiency at which crosslinking and decomposition compete with each other and to the molecular weight distribution of the resist (Reference 10).

Resolution

Resolution is usually indicated by the minimum line width that can be developed in a given layer. This will depend on the resist thickness, line-to-line spacing, beam accelerating voltage, and exposure charge density (Reference 19). For good resolution a resist with high contrast is desirable. However, even if the "latent image" formed by altered molecular structure is well defined and possesses very high resolution potential, poor developing behavior can seriously degrade resolution performance. The selection of a good developer for high resolution work is aided if the resist shows high contrast and if the insoluble fraction has good mechanical properties which minimize swelling and distortion (Reference

16) To capitalize on the ultimate high resolution capability of electron-beam lithography the edge acuity and resolution should be compatible with the writing and etching techniques and not be limited by the resist.

Molecular Weight

One of the most important parameters of a polymer resist is the average molecular weight of the polymer for both negative and positive resists.

Negative Resists. It has been well established that the interface gel dose, D_g^i , the minimum incident dose necessary to form the first insoluble gel, is inversely proportional to the intrinsic viscosity, \bar{h} , a function of the molecular weight of a negative polymer resist (Reference 6). Intrinsic viscosity is given by

$$\bar{h} = K \bar{M}_w^a$$

where K and a are constants and \bar{M}_w is the average molecular weight. For a polymer to form an insoluble gel, an average of one crosslink per chain is required. The $D_g^i \bar{M}_w$ product is a constant and is a characteristic of the polymer. For better efficiency, a polymer with small $D_g^i \bar{M}_w$ is preferred over one with a large $D_g^i \bar{M}_w$; and a polymer of high \bar{M}_w is preferred over the same polymer of low \bar{M}_w , since a polymer of higher molecular weight will have fewer chains per unit volume of film and hence require a smaller electron dose to reach a given crosslink density. Brewer (Reference 20) found that, at high molecular weights, electron sensitivity of negative resists is not a linear function of molecular weight.

Positive Resists. The efficiency of a positive electron resist is not affected by \bar{M}_w , if \bar{M}_w of the original polymer is sufficiently large (Reference 6, 18, 21, and 22) and high electron dosage is used. It depends only on the number of the average molecular weights of the fragmented polymer. However, at lower exposure dosage the \bar{M}_w of the original resist material has a very significant effect on the resist sensitivity (References 19 and 23). Harris (Reference 24) has reported that increasing the molecular weight reduces pinhole generation during development and improves edge definition, but causes a decrease in overall etch resistance, adhesion, and film quality.

Molecular Weight Distribution

Molecular weight distribution of a polymer resist has a great effect on the performance of both negative and positive electron resists.

Negative Resists. If a polymer is monodispersed (containing only one chain size) each crosslinked chain results in the same volume of gel. However, long chains (high \bar{M}_w) in a polymer of high dispersivity form a gel with lower electron doses than smaller chains. In a polymer system with high molecular weight, dispersivity gel formation occurs over a large range of doses and hence the contrast is low. When an electron beam penetrates a polymer film coated on a surface, scattering increases the beam cross-sectional area in the film. Although the beam density decreases very rapidly along the normal to the edge of the irradiated area, molecules of very high molecular weight become crosslinked and remain on the surface after development. This creates a wide sloping bank along the edges of the

developed film pattern which reduces the ultimate resolution. The resolution can be improved by fractionating the polymer to attain a sharp cutoff in the high molecular weight region of the molecular weight distribution curve (Reference 6). Molecules of molecular weight much less than \bar{M}_w are also not desirable. They are less likely to get crosslinked and are dissolved away during development, thus increasing the probability of pinhole formation. Hence negative electron resist with high molecular weight but very narrow molecular weight distribution is recommended.

Positive Resists. The effect of molecular weight distribution is more critical for a positive resist from the standpoint of selective solubility development. When a positive resist is developed it is necessary that the unirradiated polymer remain undissolved and unaltered (or almost unaltered). Hence it is important that the molecular weight distributions of the irradiated and unirradiated polymer not overlap. The dose required to shift the molecular weight of the two polymers so that low \bar{M}_w unirradiated and high \bar{M}_w irradiated tails do not overlap, is determined by the dispersivities of both polymers; it is the dose necessary for useful electron resist exposure (References 10 and 21). It is obvious that low dispersivity, narrow molecular weight distribution with sharp cutoff at both the low and high molecular weights, will increase the sensitivity and overall performance of a given positive resist (References 10 and 23-25).

Polymer Backbone Strength

Another important molecular parameter that affects the performance of an electron resist is the resistance that a polymer offers to scission (for negative resists) and crosslinking (for positive resists) induced by radiation. For each chain fractured (in negative resist) one additional crosslink is required to repair the break and results in lower sensitivity and lower contrast, since scission can be regarded as a reverse reaction inhibiting gel formation. So a polymer with a strong backbone is required: low $\frac{G(c)}{G(s)}$ value for negative resist and high $\frac{G(s)}{G(c)}$ for positive resists (References 10 and 18).

Compatibility With Fabrication Processes

Electron beam exposure and development of resist layers is only the first step in the fabrication process. Further processing of the sample and maintenance is, in general, required.

Quality of Spin-Coated Films. The resist solution should have adequate viscosity to be able to form a uniform film with desired thickness and minimum defect density on the substrate.

Adhesion. The resist should have adequate adhesion to a variety of substrates to facilitate the process used in microfabrication. Poor resist adhesion will be detrimental to all wet chemical etching processes and metalization processes that involve plating through a resist mask.

Resistance to Etching. The electron resist material should be able to withstand most acidic and basic etching solutions employed in microfabrication processes.

Resistance to Sputter Etching or Ion Milling. This requires relatively low sputtering rates of the resist material in comparison to the material being etched. The resist should also be resistant to heating.

Resistance to Heating. This is particularly important in additive metallization processes, such as the "lift-off" evaporation or sputter deposition process, and sputter etching or ion milling during which substrate surface temperature can exceed 100°C. Any resist flow at this temperature will cause image distortion and will prevent completion of the process.

Process Tolerance. The resist should not be sensitive to small daily process variabilities.

Shelf Life. The resist in both solution and spun films should exhibit adequate shelf life; typically three months or more are considered adequate. The glass transition temperature of the resist must be above room temperature, preferable above 350°K.

MATERIALS USED AS ELECTRON RESIST

Materials that have been evaluated for use as electron resists are reviewed in the paragraphs that follow.

PHOTORESIST

The first materials evaluated for use as electron resists were commercially available photoresists: Kodak Photoresist (KPR), Kodak Metal Etch Resist (KMER), Kodak Ortho Resist (KOR), and Kodak Thin Film Resist (KTER), all negative resists; and Shipley AZ 1350, a positive resist (References 1 and 26-28). These materials are readily available, processing details such as baking, developing, etc., well understood, and all have adequate resistance to common etchants. However, the photoresists are less than satisfactory as electron resists due to several deficiencies such as poor electron sensitivity, low contrast, inadequate resolution, and unnecessary sensitivities to ambient light. Because of the high sensitivity of the resists to ultraviolet light and even visible light, some chemical reactions occur on standing. Furthermore, in projection electron lithography the complete wafer is exposed using a complete pattern of electrons by employing as an electron source a photocathode that is sensitive to ultraviolet light. In this case the resist is exposed to the electrons with a background of strong ultraviolet light. Photoresists cannot be used, and electron-beam resists that are insensitive to ultraviolet light are needed. Photoresists are not stable and shelf life is short. Since their resolution deteriorates with age and varies from batch to batch, they are not satisfactory in the fabrication of devices of very small dimensions.

POSITIVE ELECTRON RESISTS

Poly(Methyl Methacrylate) (PMMA)

PMMA, a well-known thermally degrading polymer, was the first polymer reported for use, specially as an electron resist, by the IBM Watson Research Center, Yorkton Heights, N.Y. (Reference 2). PMMA was used and explored extensively during the last year (References 2, 4, 8, 9, 14, 15, 18-24, and 29-44). It has been used as a medium for comprehensive analysis of any degrading-type material and of physical and chemical properties when used as an electron resist. PMMA is insensitive to exposure by white or ultraviolet light, its synthesis is easy, it has high resolution capability ($<0.1 \mu\text{m}$) (Reference 4), good resistance to common acid and base etching processes, and is useful also as a

for ion-beam sputtering as well as for ion implantation (References 45, 46, and 47). The sensitivity of the resist is approximately $5 \times 10^{-5} \text{ C}\cdot\text{cm}^{-2}$. The resist is prepared by dissolving the polymer in its solvent (usually methyl isobutyl ketone (MIBK)). Its thickness after spin coating at over 4,000 rpm is a function of solution concentration. At 5,000 rpm and 10% solution, the thickness is $0.5 \mu\text{m}$. The resist-coated samples have to be prebaked at 170°C for 20 minutes before exposure to completely evaporate the solvent and to improve adhesion and resistance to chemical etching and resist sensitivity. Undercutting in the resist, i.e., the widening of the bottom of the trough and the width of the top of the trough, is a common phenomenon with positive resists (References 15, 21, 29, 30, 32, 34-36, 40, and 41).

This fact can cause a serious problem when narrow lines (width of the same magnitude as depth) are desired. Postbaking at 130°C for 30 minutes can eliminate this difficulty. On the other hand, there are some applications to the undercut effect: (1) high resolution is attainable using the "lift-off" process (References 29, 30, and 32), and (2) the effect is helpful in studying the energy dissipation profile of electrons in polymers, particularly in PMMA (References 15, 21, 33, 34, 39, and 42). Stripping off the exposed resist is accomplished by soaking in acetone or ethyl acetate for approximately 5 minutes. A typical resolution of PMMA is about $0.5 \mu\text{m}$ and edge definition is better than $0.05 \mu\text{m}$ with a $1\text{-}\mu\text{m}$ -thick resist.

Many publications deal with the sensitivity of PMMA as a function of exposure density, acceleration voltage, depth in resist, original molecular weight, and developing condition (composition, concentration, and temperature). Mathematical models have been assumed and theoretical calculation with experimental studies were carried out to explain the energy dissipation profile of electron penetration in PMMA and the developed resist profile (References 8, 15, 22, and 33-42).

Shimizu *et al* (References 34 and 36) used the Monte Carlo technique to simulate the energy dissipation of electrons incident onto PMMA. Greeneich and Van-Duzer (Reference 15) presented a mathematical model for the exposure of electron resist where the contribution from the primary and scattered electrons were calculated separately. They found that the controlling parameter for the primary electron contribution is the number of elastic events, where the important parameters for the scattered electrons are the backscattering coefficient and the electron range in the substrate.

By performing Monte Carlo calculation, Hawryluk *et al* (Reference 38) determined the spatial distribution of energy dissipated in a $0.4\text{-}\mu\text{m}$ -thick film of PMMA due to an incident electron beam. The effect of varying the beam diameter from 0.025 to $0.3 \mu\text{m}$ was evaluated. A detailed comparison was made between the results of the Monte Carlo calculations and analytic models that were used to predict energy dissipated. Kyser and Viswanathan (Reference 42) extended the Monte Carlo simulation techniques to the case of a laterally distributed electron beam. Equienergy density contours in the resist exhibit a size effect, i.e., dependence on the line width written. Large line widths will have a large energy density deposited in the resist because of superposition of backscattered electrons, for the same incident dose. This results in a larger solubility rate for the wider lines than for narrower lines. Hatzakis and Ting (Reference 8) made a simulation of the developed resist profile and mentioned that the profiles are not necessarily equal to the energy dissipation profiles, especially in the case of relatively high exposure density used in high speed electron beam microfabrication where the effect of the development process has to be taken into account. Ersoy (Reference 37) developed a model to account for the observed behavior of positive resists. He considered both exposure and development as a whole.

The theoretical considerations mentioned above are in good agreement with the experimental observations reviewed below.

Wolf *et al* (Reference 4) measured the electron beam energy dissipation profiles in PMMA for different exposure densities and acceleration voltages of 5,000, 10,000, 15,000 and 20,000 volts. It was

found that the 10,000-volt exposure produced the widest line in a thick resist after development in a 1:3 mixture of MIBK and 2-propanol, and that the volume of resist that was affected increased with the dose. The 10,000-volt anomaly is not really anomalous when electron energy dissipation in a solid is considered in more detail. With an electron beam with near zero energy, the energy dissipation range in the resist layer is very short and all the energy is lost within a few hundred angstroms of the surface. When electrons with higher energy are used, more energy is dissipated in the resist layer and a wider line is produced. But after progressing through some maximum line width, perhaps at about 10,000 volts, the energy dissipated is distributed deeper into the substrate with less effect on the resist layer.

Ting (Reference 33) determined the sensitivity of the PMMA resist by measuring the resist thickness as a function of development time (the solubility rate) for various exposure densities. It was found that the solubility rate not only changes with exposure density, but also with the distance from the surface at any given exposure. This nonlinear behavior at a given exposure is due to the fact that energy loss of electrons in a solid is not uniform, i.e., an electron scattering in a solid yields an energy dissipation curve which has a peak below the resist surface at approximately 0.4 of the penetration range. It was established experimentally that the solubility rate of PMMA resist changes when the exposure density is raised to the power of 1.3. From the empirical formula, one can calculate the thickness-versus-time curves for any exposure density and resist thickness. Calculated results were in very good agreement with the measured results.

Greeneich (References 35 and 44) calculated the time evolution of exposure contours in PMMA for several time-dependent developers comprising various proportions of MIBK and isopropyl alcohol (IPA). The following conclusions were reached:

1. The more active the developer (more MIBK) the greater the influence of developer time on the contours. Thus, a ratio of 1:3 of MIBK to IPA is relatively insensitive to development time compared to MIBK.
2. The energy of the incident beam is important; higher beam energies confine the penetrating beam closer to the beam axis, resulting in developed contours closer to the axis and less sensitive to development time.
3. The incident dose is particularly important. To obtain the undercut phenomenon for MIBK at low dose a large development time is required, with a corresponding increase in line width and a reduction in thickness of the original resist.
4. Increasing the temperature of the developer results in reducing the required development time for a given exposure contour.
5. The polymer's original molecular weight influences both the shape of the developed contours and the development time, but these effects are secondary to changes in the incident dose or beam energy. Furthermore, for certain values of original molecular weight, the most meaning quantity is the average number of the fragmented molecular weight (Reference 22).

Greeneich (Reference 22) established that the solubility rate of PMMA in MIBK at a given temperature is only a function of the fragmented molecular weight. For a given solvent developer, the relative solubility of the irradiated region compared to the nonirradiated region determines the contrast of the developed pattern. Hence the developer's suitability in device processing to obtain a high contrast for a given exposure density. A high molecular weight polymer is thus preferred over a low molecular weight polymer at the expense of longer development time.

Ersoy (Reference 37) found that the developed depth in PMMA increased with development time, but a time is reached where maximum depth is observed. Further development will reduce this depth because the unexposed and exposed regions develop simultaneously. Solubility changes with developer

concentration. Development saturation is a strong function of film thickness, and complete development time varies inversely with charge density.

Hatzakis (Reference 43) presented a simple procedure for evaluating the performance of any positive electron resist. The method gives a unique exposure charge-density point for optimum resolution for a given resist system independent of developer strength.

A variety of semiconductor devices and masks have been fabricated by electron beam lithography using PMMA resist to demonstrate not only high resolution lithography, but also to show that adequate associated processes exist for making properly functioning devices. The devices include: bipolar transistors (References 32, 48, 49, and 50), acoustic surface wave transducers and filters (References 4, 29, 51, and 52) with line widths less than 0.5 μm , 1024-bit random access memory chips (Reference 53), microwave transistors (References 45 and 54), integrated field-effect transistors (References 46, 55, and 56), integrated circuit metal oxide semiconductor (MOS) field-effect transistors with 8,000-bit memory chips (Reference 57), master masks (Reference 30), and more.

Modified PMMA Electron Resists

PMMA has definite restrictions in its use as a resist material.

1. Its sensitivity is low, approximately $5 \times 10^{-5} \text{ C}\cdot\text{cm}^{-2}$, for economical use in large-scale fabrication of devices, and is limited by the relatively small change in dissolution rate after irradiation at low exposures. The low sensitivity is related to the low $G(s)$, $G(s)$ being approximately equal to 2, the number of main chain fractures per 100 electron volts of energy absorbed.

2. It is rather difficult to control the development of a very fine pattern.

3. The developed film pattern is thermoplastic and can be deformed easily if the film becomes heated during processing, particularly in applying the "lift-off" technique or in ion milling and sputter etching.

Several suggestions have been reported to improve the performance of PMMA resist by incorporating different modifications in the resist system.

1. Roberts (References 58 and 59) reported that a modified PMMA system, thermally crosslinked after application to the substrate, exhibited a sensitivity of 8 to $40 \times 10^{-6} \text{ C}\cdot\text{cm}^{-2}$ as a positive resist. The amount of sensitivity was dependent upon the degree of crosslinking in the film. The material has better etch and solvent resistance than PMMA, especially to ion-beam etching, and provides films having thermal stability superior to that of PMMA. The resist withstands temperatures of more than 100°C higher than that which PMMA will tolerate before thermal deformation can be detected. It allows the lift-off technique to be operated with a wider range of metals than was found possible with PMMA. Efforts to improve the thermal stability of PMMA have also been done at Hughes Research Laboratories, Malibu, Calif.

2. Copolymers of methyl methacrylate and acrylonitrile have been investigated as a positive electron resist (Reference 60). A copolymer resist with 7-mole percent of acrylonitrile can be patterned at an electron exposure of $5 \times 10^{-7} \text{ C}\cdot\text{cm}^{-2}$ using a 1:9 mixture of ethanol and isomyl acetate. Variations in the copolymer composition make it possible to use a developer of a single composition.

3. Gipstein *et al* (Reference 61) attempted to improve the sensitivity and adhesion of PMMA by copolymerization with isobutylene. The glass transition temperature of polyisobutylene (PIB) is low (-70°C), but copolymerization of isobutylene with methyl methacrylate will significantly raise the T_g of PIB above room temperature, and the PMMA resist sensitivity may be enhanced by incorporating more

radiation sensitive links that exist in PIB. The van der Waals adhesion of PMMA would also be enhanced by incorporating the elastomeric isobutylene unit. PMMA isobutylene copolymers containing 10-25% units of isobutylene were found to have better performances than PMMA as electron resists; the 75:25% copolymer as sensitive as $5 \times 10^{-6} \text{ C}\cdot\text{cm}^{-2}$. Brewer (Reference 20) found that adding energy-transferring type sensitizers had very little effect on the sensitivity of PMMA.

Polysulfones

Polysulfones have been shown to have high $G(s)$ values (7-10) (Reference 62), making them candidates for use as positive electron resists. Bowden and Thompson (References 63-68) have shown that polysulfones constitute a family of alternating copolymers of SO_2 , and that an olefin can be degraded readily in an electron beam and serve as good positive electron beam resists with a sensitivity of approximately $2 \times 10^{-6} \text{ C}\cdot\text{cm}^{-2}$ (Reference 66). The sensitivity depends on the olefin structure, exposure temperature, accelerating voltage, and molecular weight. In addition to chain scission under electron irradiation, a second reaction can occur to amplify the scission process, namely chain depropagation. This results when two polymer radicals, formed by chain scission, spontaneously split off to monomer units. The extent of chain depropagation depends on the rate of radical termination and the rate of depropagation. If the polymer chain completely depolymerizes, the film will be totally removed, thereby eliminating a solvent development step. This process is termed "vapor development." Hence, the polysulfone may be used in two development modes; firstly, as a conventional solvent-development system; and secondly, under proper conditions, as a solvent-free, vapor development. The vapor development process is inherently interesting because it eliminates the necessity for a "wet" development process. The rate of vapor development depends markedly on the olefin structure (Reference 67) and exposure temperature. Vapor development may find some use in special applications. But for microcircuit fabrication it has been shown not to be a versatile technique due to difficulties in removing the last 10% of the film (References 64 and 67-69), thus making subsequent etching variable. In addition, since in the vapor development process radicals are being formed continually during electron irradiation, the product gases can contaminate the writing machine. Hence, for microcircuit fabrication, conventional solvent development is preferred.

The solvent developed sensitivity of all the polysulfones of equivalent molecular weight was found to be 2 to $4 \times 10^{-6} \text{ C}\cdot\text{cm}^{-2}$ at 10,000 volts. Hence, choice of a particular polysulfone as a resist is determined by considering film-forming properties, etch resistance, low rate of vapor development, etc. Poly(butene-1-sulfone) has been chosen as a promising sulfone resist system according to these considerations; furthermore, it has excellent overall resist properties. By carefully controlling molecular weight, molecular weight distribution and polymer dissolution mechanisms, a sensitivity of $7.8 \times 10^{-7} \text{ C}\cdot\text{cm}^{-2}$ can be achieved (Reference 65). One serious drawback of the olefin sulfones, however, is the poor resistance to ion milling or backspattering. Poly(styrene sulfone) (Reference 70) was found to be resistant to ion etching but with a decrease in sensitivity to $1 \times 10^{-5} \text{ C}\cdot\text{cm}^{-2}$ (still higher than PMMA) as a positive resist.

The development of poly(butene-1-sulfone) was held up by an unknown source of pinholes in etched chrome patterns (for master mask). By filtering three times through a $0.2\text{-}\mu\text{m}$ filter the density of the pinholes was reduced markedly, however.

Himics *et al* (References 17 and 71) reported on several functionally substituted olefines, including cyclopentene and cyclohexene, that have been copolymerized with SO_2 as positive electron beam resists.

The sensitivity of poly(cyclopentene sulfone) was found to be $2.6 \times 10^{-5} \text{ C}\cdot\text{cm}^{-2}$. This resist gave a straight-walls relief after development. For only one material, poly(5-hexene-2,1-sulfone), was a solvent found in which the exposed and unexposed portions of the film exhibited a moderately large differential solubility.

Poly(Methyl Isopropenyl (Ketone)) – PMIPK

Levine *et al* (Reference 72) reported on polymers of methyl isopropenyl ketone as positive electron resists. Sensitivities of polymers with several vinyl monomers were determined. Information relevant to the mechanism of depolymerization was obtained by comparing homopolymers with copolymers and by the use of additives in the irradiated polymer films. It was shown that the primary mechanism for PMIPK degradation by electron irradiation is not a free radical in nature. The sensitivity reported was 2×10^{-5} to $2 \times 10^{-6} \text{ C}\cdot\text{cm}^{-2}$. PMIPK is compatible with buffered HF and KI/I_2 etchants, can be used in liftoff processing, and has good adherence to SiO_2 , Cr and Au. The polymer is apparently attacked by alkaline etchants making Cr photomask production difficult.

Other Positive Electron Resists

Other positive electron resists have been reported: poly(methyl styrene) (Reference 6), cellulose acetate, cellulose triacetate, polyacetal, polyisobutylene, and vinyl ester polymer (Reference 20). But they are less attractive as the resists described above.

NEGATIVE ELECTRON RESISTS

Cross-section profiles of single-scan negative electron-resist lines were considered theoretically by Heidenreich *et al* (Reference 73) and Lin (Reference 74). Heidenreich *et al* used the depth-dose theory of electron energy dissipation in negative electron resist (Reference 13) and a quasimono-energetic Gaussian scattering theory (Reference 19) to derive theoretical expressions for single-line profiles using the exposure parameters of the exposure system. Those profiles were calculated by convoluting the Gaussian scattering distribution with the experimentally determined relationship between resist thickness remaining after development and input-electron dose. The results showed the importance of good gel rigidity and high contrast required for negative electron resists used in high resolution applications. Their calculations led to the choice of optimum exposure for the exposure system. However, the analytical expression in the consideration above contains parameters which are not readily obtainable for an arbitrary combination of resist and substrate. Lin (Reference 74) presented a method of calculating negative resist-line profiles from parameters which are all experimentally measurable. The method is based on the measurement of the beam current density distribution inside the resist film and on the measured contrast and minimum dose required for resist development. The profile was found to be parabolic when the exposure dose, the initial film thickness, and the beam radius in the resist film were properly chosen.

Thompson *et al* (Reference 3) studied the use of low-voltage exposure of negative electron resists. The use of 5,000 to 20,000 accelerating volts was found to be advantageous. The decrease in critical

dose with decreasing accelerating voltage was demonstrated. This increase in sensitivity was shown to be due to increased energy dissipation in the resist film (Reference 13). The major factor that limits the lowest practical voltage is the penetration of the electron beam through the resist. The effect of dose and accelerating voltage on line width was studied, too. It was found that the exposed line width is dose dependent, and if high resolution patterns are required, the critical dose for crosslinking should not be exceeded. It was also found that overexposure can cause a chemical degradation of the resist film. The effect of accelerating voltage on line width pertains to the transverse scattering effect (Reference 13): the line width of a pattern increases with voltage. The advantage in working at low accelerating voltages was clearly demonstrated.

Epoxide-Containing Negative Electron Resists

High sensitivities to electron beams have been found in epoxide-containing polymers (References 3, 10, 12, 23 and 75-79). The glycidyl or epoxy group are found to be a very satisfactory chemically reactive species for negative electron resists. This group has a high radiation susceptibility and can be easily incorporated into a wide variety of polymers.

Epoxidized 1-4 Polybutadiene. (References 76 and 77). This resist has a high sensitivity: approximately 10^{-7} C·cm⁻² at 15,000 volts. In the range of 5,000 to 20,000 volts, the sensitivity increases with decreasing accelerating voltage and increasing molecular weight of the polymer. The relationship between the sensitivity and the degree of epoxidation of the polymer was found and can be explained accurately by assuming that the insolubilization process of the polymer involves a chain reaction mechanism. Thin films of the polymer insolubilize slowly, even in the absence of irradiation. However, this phenomenon can be eliminated by adding a small quantity of some kind of stabilizer to the polymer (Reference 76). It was found that epoxidized 1-4 polybutadiene exhibited very poor contrast and inadequate shelf life, and when initial films of greater than 0.6 μ m were used, considerable loss of resolution resulted (Reference 10).

Crosslinking Electron Resist. A crosslinking electron resist reported by Thompson *et al* (Reference 3) and based on a terpolymer of methyl methacrylate, ethyl acrylate and glycidyl methacrylate, partially esterified with methacrylic acid. It was found to have a sensitivity of approximately 8×10^{-7} C·cm⁻² and excellent contrast with adequate adhesion, resolution, and etch resistance. But a complex preparation required to obtain the polymer in a high molecular weight form is a disadvantage.

Poly(Glycidyl Methacrylate-co-Ethyl Acrylate) (P(GMA-co-EA)). (References 10, 12, 78, and 79). Poly(glycidyl methacrylate) (PGMA) (Reference 79) of high molecular weight (M_w approximately 10^6) is more sensitive than epoxidized 1-4 polybutadiene (M_w approximately 10^4) (Reference 3); however, it has less than satisfactory adhesion to most substrates and is not a good resist material. The physical and chemical properties of PGMA are easily modified by copolymerization with a variety of other monomers. Copolymerization may result in a decrease in the bulk electron sensitivity, but some sacrifice in this property is possible in order to optimize other resist properties. Ethyl acrylate was selected by Thompson *et al* (References 78 and 79) as a comonomer because of its low glass transition temperature and excellent thin film properties. The application of P(GMA-co-EA) (68% GMA and 32% EA) is a very good negative resist for electron beam lithography as far as physical and chemical properties are concerned.

1. The dose required to achieve 70% of the initial film remaining is 2×10^{-7} C·cm⁻², and the material exhibits a higher contrast than epoxidized 1-4 polybutadiene which is of comparable sensitivity. An accelerating voltage of 5,000 volts is optimum for an initial film thickness of 0.5 μ m. It is believed

this sensitivity is adequate for most applications. The sensitivity of P(GMA-co-EA) can be varied by changing either the molecular weight or the glycidyl methacrylate content.

2. The polymer, when prebaked, adheres tenaciously to metal and SiO_2 substrates.
3. The copolymer resists both acid and basic chemical etching solutions and argon ion etching.
4. At the stated temperatures, the resist film is insensitive to large changes in the duration of prebake and postbake.
5. The useful life of the coated and prebaked resist exceeds 24 hours.
6. The total processing from coating to stripping requires no new processing steps. The resist can also be stripped by plasma of O_2 wet air and CH_4 .
7. The minimum-feature size obtained for the fabrication of optical gratings was $\leq 0.3 \mu\text{m}$, and $< 0.5 \mu\text{m}$ for continually etched metals and dielectrics.

Pease *et al* (Reference 80) used P(GMA-co-EA) to make a high-quality photographic master mask in which lines and spaces of $1.0 \mu\text{m}$ were resolved, and also to make MOS integrated circuits with improved packing density and performance.

Poly(Glycidyl Acrylate-co-Styrene) (P(GA-co-S)) and Poly(Glycidyl Metacrylate-co-Styrene) (P(GMA-co-S)). (Reference 23) Rai *et al* (Reference 22) reported on synthesis and evaluation of copolymers of styrene and epoxide-containing monomers. P(GA-co-S) showed a sensitivity of 2.9×10^{-6} to $2.5 \times 10^{-7} \text{ C}\cdot\text{cm}^{-2}$ and P(GMA-co-S) showed a sensitivity of 1.2×10^{-5} to $5.0 \times 10^{-6} \text{ C}\cdot\text{cm}^{-2}$. Both exhibited satisfactory resistance to sputter etching.

Polysiloxanes

Several polysiloxane polymers have been reported as negative electron resists exhibiting sensitivity values of 5×10^{-4} to $1 \times 10^{-6} \text{ C}\cdot\text{cm}^{-2}$ (References 81-85). They can be thermally converted to SiO_2 with good dielectric properties for integrated circuits application, thereby eliminating liquid etching techniques.

Yatsui *et al* (Reference 81) reported that methylvinylpolysiloxane has a sensitivity of $8.8 \times 10^{-7} \text{ C}\cdot\text{cm}^{-2}$ at 10,000 volts. It was shown that flood-beam irradiation (10^{-4} to $10^{-5} \text{ C}\cdot\text{cm}^{-2}$) on the developed resist film, corresponding to the post-bake process, was effective in increasing the chemical resistance and adhesive force to the substrate. Such resist is useful to practically all etchants other than H_2SO_4 . It was found that the resist dissolves very little in buffered HF, and that SiO_2 of $0.3 \mu\text{m}$ was successfully etched without damaging the resist film. The resists showed decreasing sensitivity on the order of those having vinyl groups, methyl groups, and phenyl groups. When a more sensitive siloxane resist is required, one containing phenyl groups must be avoided.

Roberts (References 82 and 83) reported on polymethylcyclsiloxane (PMCS) as a resist in which a siliceous film pattern may be formed by irradiation with an electron beam. The siliceous patterns are readily developed and may be used directly in semiconductor technology as diffusion barriers or as etch-resistant layers. After suitable heat treatment they also may be used as passivating layers. The sensitivity of PMCS to electron beam irradiation may be increased by controlled condensation to give a higher molecular weight polymer, or by introducing vinyl groups in the polymer. It was shown that at doses normally used, crosslinking occurs mainly through the hydroxyl groups present in the polymer. Subsequent thermal or radiation treatment can eliminate organic residues to produce a film which is identical to thermally grown silica. Roberts (Reference 83) reported on overcoming instability in MOS structures. The instability was attributed to the presence of positive ions in the oxide and was overcome

by applying a thin layer of a mixture of cyclosiloxane polymer with an organosilylene phosphate in a pattern defined by an electron beam. The mixture may be converted by subsequent heat treatment to phosphosilicate glass.

Gazard *et al* (References 84 and 85) reported on three negative siloxane resists: polymethylsiloxane (PMS), polyvinylsiloxane (PVS) and polyphenylsiloxane (PPS). The sensitivity of PVS was the highest: $5 \times 10^{-6} \text{ C}\cdot\text{cm}^{-2}$. PVS and PMS are transformed to silica when postbaked at 800°C and can be used as an insulating layer and barriers for diffusion and ion implantation. The possibility of using PPS to fabricate optical waveguide in integrated optics was demonstrated.

Poly(Diallylorthophthlate) (PDOP)

Bartelt (Reference 86) reported that the polymer PDOP serves as a thermally stable electron resist with a sensitivity of $1 \times 10^{-6} \text{ C}\cdot\text{cm}^{-2}$. PDOP has excellent adhesion to metals and SiO_2 , fine resolution, good etch resistance and thermal stability, so is especially useful in patterning processes requiring high thermal stability. Pease *et al* (Reference 80) used PDOP to make high-quality photolithographic master masks in which lines and spaces of $1.0 \mu\text{m}$ were resolved, and also to make MOS integrated circuits with improved packing density and performance.

Other Negative Electron Resists

Ku and Scala (Reference 6) described the properties of three negative electron resists: polystyrene, poly(vinyl chloride) (PVC) and polyacrylamide. Polystyrene is resistant to all alkalis and weak acids, but is attacked slowly by strong oxidizing acids. PVC is resistant to most acids, alkalis, and common inexpensive organic solvents. Irradiation in air causes degradation, but irradiation in a vacuum induces crosslinking. Polyacrylamide is a water solution polymer. The sensitivity is about $5 \times 10^{-6} \text{ C}\cdot\text{cm}^{-2}$. The crosslinked polymer is not soluble in water, but is swelled by aqueous solutions such as buffered HF, dilute acids, and alkalis. Hence, polyacrylamide is not an etch resist for aqueous acids or alkalis. The crosslinked polymer is resistant to concentrated phosphorous acid and is, therefore, a useful aluminum etch resist. It may also be used as a mask for sputtering etch.

Cole *et al* (References 87 and 88) reported on electron resists prepared by the reaction of vinyl ether-maleic anhydride copolymers with various alcohols. The allyl half-ester of an octadecylvinylether-maleic copolymer was stable, and formed excellent films with a sensitivity of $4 \times 10^{-8} \text{ C}\cdot\text{cm}^{-2}$ at 9,000 volts. The exposed and developed resist pattern, while being insoluble in an adherent, will not resist acid etchants without a short heat curing cycle. Bulk material and spun films are stable for more than one year. They have shown that terminal unsaturation is required for high electron sensitivity. Displacement of the unsaturation to a position other than terminal causes a marked loss in sensitivity. There is a direct association between the electron sensitivity and the presence of the ether group. Removal of the ether group causes a sharp loss in sensitivity and furthers the presence of an aromatic group which results in resists with even less sensitivity. It is likely, therefore, that the most efficient radiation induced crosslinking reactions are activated through the unsaturated terminal group and that the ether side chain allows a very efficient side for the reaction.

Paal *et al* (Reference 89) described copolymers of methacrylate and acrylate esters containing polymerizable double bonds as electron resists. The sensitivity was approximately $3 \times 10^{-7} \text{ C}\cdot\text{cm}^{-2}$.

Brewer (Reference 18) evaluated a large number of polymers as to their electron irradiation sensitivities and contrasts. Results indicate that the sensitivity of negative resist increases proportionately with the number of vinyl groups.

Polyvinylpyrrolidone (PVP) is a negative electron resist with a sensitivity of approximately $2 \times 10^{-6} \text{ C cm}^{-2}$ and very high resolution capability ($\leq 0.1 \mu\text{m}$). The resist is developed by deionized water; however, an apparent swelling of the resist pattern, in high resolution, was found.

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